Test of variational transition state theory against accurate quantal results for a reaction with very large reaction-path curvature and a low barrier

Donald G. Truhlar
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Bruce C. Garrett
Chemical Dynamics Corporation, 1550 West Henderson Road, Columbus, Ohio 43220

Paul G. Hipes and Aron Kuppermann
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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We present three sets of calculations for the thermal rate constants of the collinear reaction $I + HI \rightarrow IH + I$: accurate quantum mechanics, conventional transition state theory (TST), and variational transition state theory (VTST). This reaction differs from previous test cases in that it has very large reaction-path curvature but hardly any tunneling. TST overestimates the accurate results by factors of 2×10^{10}, 2×10^{4}, 57, and 19 at 40, 100, 300, and 1000 K, respectively. At these same four temperatures the ratios of the VTST results to the accurate quantal ones are 0.3, 0.8, 1.1, and 1.4, respectively. We conclude that the variational transition states are meaningful, even though they are computed from a reaction-path Hamiltonian with large curvature, which is the most questionable case.

I. INTRODUCTION

Variational transition state theory (VTST), with an approximate treatment of the effects of quantization,[1-4] has now been applied to chemical reactions with a variety of mass combinations and potential energy surfaces. A general conclusion is that the largest deviations of the predicted rate constants from those of conventional transition state theory are associated with symmetric or nearly symmetric systems with a light atom being transferred between two much heavier partners; this was originally concluded on the basis of semiempirical potential energy surfaces,[1-10] and a similar trend has been observed using surfaces based on *ab initio* calculations.[11,12] The predictions of VTST for this kind of system have been checked against experiments for the H/D kinetic isotope effect in $^{37}Cl + H\,^{35}Cl \rightarrow H\,^{37}Cl + {}^{35}Cl$[12] and against accurate quantal reaction probabilities for collinear $Cl + HCl \rightarrow ClH + Cl$.[10] For the latter study accurate quantal scattering calculations and VTST calculations were carried out using the same London–Eyring–Polanyi–Sato (LEPS)-type[13] potential energy surface in order that the comparison of rate constants provides a test of VTST's ability to predict rate constants for a given (realistic) potential energy surface.[10] The test showed that the predictions of VTST, when an appropriate transmission coefficient[12] to account for tunneling is included, are in good agreement with the quantal rate constants. In this article we report a similar comparison of VTST predictions to accurate quantal results, this time for the collinear reaction $I + HI \rightarrow IH + I$. At a given temperature tunneling effects are less important in the present system than in the $Cl + HCl$ system. Thus the present calculation provides a more direct test of the variational choice of the transition state for the over-barrier contribution to the rate constant.

II. CALCULATIONS

A. System

The system is specified by the masses ($m_I = 231\,325 m_e$, $m_H = 1837 m_e$) and the potential energy surface. The surface is based on the popular extended LEPS formulation[14] with Morse parameters and Sato parameters given in a previous publication,[15] where it is called surface *a*. This surface has a symmetric saddle point at $R_{HI} = 3.366 a_0$ with a classical barrier height of 1.353 kcal/mol.

B. Quantal rate constants

Accurate fixed-energy reaction probabilities were calculated by solving the coupled-channel equations in hyperspherical coordinates. The reaction probability as a function of energy has already been reported.[15] To calculate converged thermal rate constants over a wide temperature range, additional fixed-energy reaction probabilities were calculated and the results were thermally averaged.

In the course of these calculations an interesting low-energy resonance was discovered. This resonance has only a very small effect on the thermal rate constants, and it will be discussed in more detail in a subsequent publication.[16]

The accurate quantal rate constants are given in Table I.

C. Generalized transition state theory

The methods used for the generalized transition state theory calculations with classical reaction-coordinate motion are the same as we applied to the $Cl + HCl$ reaction.[12] In particular all vibrational partition functions are based on the Morse I approximation,[1] and the rate constant is calculated by improved canonical variational theory (ICVT).[2]

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TABLE I. Accurate quantal rate constants.

T(K)	k (cm molecule^{-1} s^{-1})
40	7.03(2)[a]
60	1.23(3)
100	2.12(3)
200	3.89(3)
300	5.26(3)
400	6.31(3)
600	7.69(3)
800	8.55(3)
1000	9.17(3)

[a] Number in parentheses is a power of 10.

Quantal effects on the reaction-coordinate motion are included by the large-curvature, ground-state (LCG)[12] approximation for the transmission coefficient. For comparison we also present results obtained by some alternative procedures. One alternative procedure is to use the WKB approximation instead of the Morse I approximation for the ground-state stretching vibration of the reactant and generalized transition states.[17] This tests the effect of using the true vibrational potential in the generalized-transition-state dividing surface without modifying its shape. In addition we report calculations in which we neglected the transmission coefficient (i.e., set it equal to unity), and in which we calculated it in the small-curvature-tunneling semiclassical adiabatic ground-state (SCTSAG)[18] approximation, by two alternative versions (LCG2[10] and LCG3[19]) of the large-curvature ground-state method, and by the least-action ground-state (LAG)[20] approximation. The transmission coefficients account for quantum mechanical tunneling and nonclassical reflection effects as discussed elsewhere.[12,18–20] Additional calculations were performed using canonical variational theory (CVT[1,2]) and CVT combined with the classical adiabatic ground-state (CAG[2]) transmission coefficient.

The approximate rate constants are compared to the accurate ones in Tables II and III. Both tables include results obtained treating the bound stretching vibrations by the Morse I approximation and also by treating the ground-state stretching vibration by the WKB approximation. Table II shows results obtained by conventional transition state theory with unit transmission coefficient (denoted ‡), by conventional transition state theory with Wigner's lowest-order quantal transmission coefficient[1,8,21] (denoted ‡/W), by CVT and ICVT, and by ICVT combined with four of the methods to calculate the transmission coefficient. Table III shows additional results obtained with ICVT combined with two of the methods to calculate the transmission coefficient.

III. DISCUSSION

First we compare the ICVT calculations with the various kinds of transmission coefficients. Tables II and III show that all methods for calculating the transmission coefficient of variational transition state theory predict a negligible quantal effect on the reaction coordinate motion, independent of the method used to treat the ground-state stretching vibration. Furthermore, over the whole temperature range considered in the present study, the CVT, CVT/CAG (not shown in tables), and ICVT rate constants agree to better than 1%. Thus, in the interpretive analysis later in this section, we will limit our discussion of the variational transition state theory results to the simplest of these theories, namely CVT with unit transmission coefficient.

Table II shows that improving on the Morse I approximation for the stretching vibration of the generalized transition state does make a quantitative improvement in the accuracy of ICVT at low temperatures where the results are most sensitive to small changes in effective energy barriers. However, in the temperature range of most general interest, 200–1000 K, the improved treatment of the stretching vibration makes a difference of 15% or less and slightly deteriorates the accuracy of ICVT, presumably indicating a small cancellation of errors contributing in part to the accuracy of the CVT calculations with the Morse I approximation. The present comparison of Morse I and WKB approximations is of special interest because large reaction-path curvature can distort the shape of the bound vibrational potentials of generalized transition states and cause the Morse I approximation to be inappropriate. The most important conclusion from the comparison of the Morse I and WKB results in Tables II and III is that even for this extreme mass combination, which contributes very large reaction-path curvature, the differences between the ICVT rate constants calculated with the Morse I and WKB approximations are small compared to typical "chemical accuracy" (say 30%) except at very low temperatures, below 100 K, where all Boltzmann factors become very sensitive to small energy differences. This indicates that the Morse I approximation is not too inaccurate at the variational transition states. For the rest of

TABLE II. Ratios of approximate rate constants to accurate quantal ones.[a]

T(K)	‡	‡/W	CVT	ICVT	ICVT/LCG	ICVT/LCG2	ICVT/LCG3	ICVT/LAG
40	1.80×10^{10}	2.86×10^{11}	0.31	0.31(0.63)	0.31	0.32	0.32	0.32
60	7.89×10^{6}	6.01×10^{7}	0.52	0.52(0.83)	0.51	0.52	0.52	0.52
100	1.75×10^{4}	5.92×10^{4}	0.77	0.77(1.02)	0.77	0.77	0.77	0.77
200	2.14×10^{2}	3.42×10^{2}	0.99	0.99(1.14)	0.99	0.99	0.99	0.99
300	5.70×10^{1}	7.21×10^{1}	1.07	1.07(1.16)	1.06	1.07	1.07	1.07
400	3.23×10^{1}	3.71×10^{1}	1.12	1.12(1.19)	1.12	1.12	1.12	1.12
600	2.13×10^{1}	2.27×10^{1}	1.23	1.22(1.27)	1.22	1.22	1.22	1.23
800	1.94×10^{1}	2.01×10^{1}	1.34	1.33(1.38)	1.33	1.33	1.33	1.33
1000	1.93×10^{1}	1.98×10^{1}	1.44	1.42(1.47)	1.42	1.42	1.43	1.42

[a] Morse I approximation for stretches except for numbers in parentheses, which are based on the WKB approximation for ground-state stretches.

TABLE III. Ratio of approximate rate constants to accurate quantal ones.

Method	ICVT/SCTSAG		ICVT/LAG	
T(K)	300	600	300	600
Morse I	1.07	1.22	1.07	1.22
WKB	1.16	1.27	1.16	1.27

the discussion we shall limit our attention to the results obtained by the simpler and more widely applied of the two approximations, namely the Morse I approximation.

Comparison of columns 2 and 4 or 5 of Table II shows that there is a very large effect of variationally optimizing the location of the generalized transition state. Conventional transition state theory overestimates the rate constants by very large factors and inclusion of the Wigner transmission coefficient makes the theory even less accurate. Clearly the Wigner transmission coefficient of conventional transition state theory does not provide a meaningful estimate of quantal effects on reaction coordinate motion when conventional transition state theory itself is so inaccurate. This is so because the Wigner transmission coefficient is based on the properties of the saddle point, and, when conventional transition state theory is so inaccurate, saddle point properties do not determine the true dynamical bottleneck. In the conventional theory the transition state is located at the saddle point, whereas in CVT and ICVT it is located to maximize the generalized and the improved generalized free energies of activation, respectively.[2,22] Either of these quantities should be maximized at a location that enhances the validity of the dynamical bottleneck assumption of transition state theory; classically this would correspond to minimizing the number of trajectories that recross the generalized-transition-state theory phase-space dividing surface separating reactants from products.[23–26]

More detailed insight into the origin of the large variational effect for the present reaction is obtained by tabulating some properties of the canonical variational transition states as functions of temperature. This is done in Table IV where these properties are compared to the same quantities evaluated at the saddle point and for reactants. The quantities in Table IV are as follows: s, the value of the reaction coordinate in coordinates[1,25] scaled to a reduced mass of $m_I m_{HI}/m_{IHI}$; R_{HI} and R_{IH}, the nearest-neighbor distances; B_F, the curvature[2] of the minimum-energy path in mass-scaled coordinates; V_{MEP}, the potential energy on the minimum-energy path; $\hbar\omega_{str}$, the harmonic frequency (in energy units) of the stretching vibration; and ΔV_a^G, the vibrationally adiabatic ground-state potential curve relative to reactants. The last quantity is defined by

$$\Delta V_a^G(s) = V_a^G(s) - V_a^G(s = -\infty),$$

where

$$V_a^G(s) = V_{MEP}(s) + \epsilon_{str}(n = 0,s)$$

and $\epsilon_{str}(n,s)$ is the quantized energy of the stretching vibration with quantum number n at s obtained by the Morse I approximation. Table IV shows that the variational transition state and its properties are not very sensitive to temperature for this system. This slight dependence on temperature results from the dominance of the ground vibrational state of the stretching vibration. At the saddle point, the reaction-path curvature is very large and this expands the distance between the potential energy contours along the mass-scaled vibrational coordinate, decreasing $\hbar\omega_{str}$ so much that ΔV_a^G is negative. At the variational transition states, V_{MEP} is much lower but $\hbar\omega_{str}$ and $\epsilon_{str}(n = 0,s)$ are much greater, close to their value at reactants, resulting in a small but positive ΔV_a^G. The reaction-path curvature and the deviation of one of the nearest-neighbor distances from its value in the reactants are both very small at the variational transition states; this accounts for the stretching frequency there being close to its reactant value.

The negative value of the ΔV_a^G at the saddle point is responsible for the serious breakdown of conventional transition state theory for this reaction. Because $\Delta V_a^G(s = 0)$ is negative, the conventional transition state theory rate constant actually decreases at low temperature, from 1.26×10^{13} cm molecule^{-1} s^{-1} at 40 K to 1.64×10^{5} cm^3 molecule^{-1} s^{-1} at 600 K. At higher temperatures it increases, reaching 2.16×10^{5} cm molecule^{-1} s^{-1} at 1000 K. In contrast the CVT rate constant increases monotonically from 2.20×10^{2} cm molecule^{-1} s^{-1} at 40 K to 9.43×10^{3} cm molecule^{-1} s^{-1} at 600 K to 1.68×10^{4} cm molecule^{-1} s^{-1} at 1000 K.

IV. SUMMARY

In previous work we have often found large differences between conventional and variational transition state theory

TABLE IV. Properties of generalized transition states and reactants.

T (K)	s (a_0)	R_{HI} (a_0)	R_{IH} (a_0)	B_F (a_0^{-1})	V_{MEP} (kcal/mol)	$\hbar\omega_{str}$ (cm^{-1})	ΔV_a^G (kcal/mol)
				Conventional transition state			
...	0.000	3.366	3.366	1.06×10^{1}	1.35	149	−1.764
				Canonical variational transition states			
40	−0.760	4.428	3.047	5.7×10^{-3}	0.513	2135	0.204
200	−0.760	4.428	3.047	5.7×10^{-3}	0.513	2135	0.204
600	−0.772	4.441	3.047	5.7×10^{-3}	0.505	2141	0.204
1000	−0.849	4.521	3.043	5.3×10^{-3}	0.456	2174	0.202
	Reactants						
...	$-\infty$	∞	3.024	0.0	0.000	2355	0.000

with quantized generalized transition states and classical reaction-coordinate motion. (We call these differences variational effects.) In the cases where the differences were largest (many orders of magnitude) we also found large quantal effects on reaction-coordinate motion. In the present article we studied a system with large differences between conventional and variational transition state theory but not large quantal effects on reaction-coordinate motion. This study confirms the reality of the large variational effects. Furthermore even when the variational effect is over nine orders of magnitude, variational transition state theory with simple, practical procedures for calculating the quantized energy levels of generalized transition states, gives quantitative estimates of the true quantal rate constants. For 100–1000 K our variational transition state theory rate constants are accurate within a factor of 1.5 or better, although conventional transition state theory is inaccurate by over four orders of magnitude at 100 K and by a factor of 19 at 1000 K.

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[1]B. C. Garrett and D. G. Truhlar, J. Phys. Chem. **83**, 1079 (1979); **84**, 682(E) (1980); **87**, 4553(E) (1983).
[2]B. C. Garrett, D. G. Truhlar, R. S. Grev, and A. W. Magnuson, J. Phys. Chem. **84**, 1730 (1980); **87**, 4554(E) (1983).
[3]D. G. Truhlar and B. C. Garrett, Acc. Chem. Res. **13**, 440 (1980).
[4]D. G. Truhlar, A. D. Isaacson, R. T. Skodje, and B. C. Garrett, J. Phys. Chem. **86**, 2252 (1982); **87**, 4554(E) (1983).
[5]B. C. Garrett and D. G. Truhlar, J. Am. Chem. Soc. **101**, 4534 (1979).
[6]B. C. Garrett and D. G. Truhlar, J. Am. Chem. Soc. **101**, 5207 (1979).
[7]B. C. Garrett and D. G. Truhlar, J. Am. Chem. Soc. **102**, 2559 (1980).
[8]B. C. Garrett, D. G. Truhlar, and A. W. Magnuson, J. Chem. Phys. **74**, 1029 (1981).
[9]B. C. Garrett, D. G. Truhlar, and R. S. Grev, in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981), p. 587.
[10]D. K. Bondi, J. N. L. Connor, B. C. Garrett, and D. G. Truhlar, J. Chem. Phys. **78**, 5981 (1983).
[11]B. C. Garrett, D. G. Truhlar, R. S. Grev, and R. B. Walker, J. Chem. Phys. **73**, 235 (1980).
[12]B. C. Garrett, D. G. Truhlar, A. F. Wagner, and T. H. Dunning, Jr., J. Chem. Phys. **78**, 4400 (1983).
[13]I. W. M. Smith, *Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, London, 1980), p. 43.
[14]P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, J. Chem. Phys. **44**, 1168 (1966).
[15]J. A. Kaye and A. Kuppermann, Chem. Phys. Lett. **77**, 573 (1981).
[16]P. G. Hipes and A. Kupperman (to be published).
[17]B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **81**, 309 (1984).
[18]R. T. Skodje, D. G. Truhlar, and B. C. Garrett, J. Chem. Phys. **77**, 5955 (1982).
[19]D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, in *The Theory of Chemical Reaction Dynamics*, edited by M. Baer (Chemical Rubber, Boca Raton, FL, 1984).
[20]B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **79**, 4931 (1983).
[21]H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966), p. 134.
[22]A. Tweedale and K. J. Laidler, J. Chem. Phys. **53**, 2045 (1970).
[23]J. C. Keck, Adv. Chem. Phys. **13**, 85 (1967).
[24]W. H. Miller, J. Chem. Phys. **61**, 1823 (1974).
[25]B. C. Garrett and D. G. Truhlar, J. Phys. Chem. **83**, 1052, 3058(E) (1979); **87**, 4533(E) (1983).
[26]B. C. Garrett and D. G. Truhlar, J. Phys. Chem. **84**, 805 (1980).